MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD

NEW POLYORGANOSILOXANES PREPARED FROM SILICATE MINERALS

Final Technical Report

By

B.R. Currell

August 1977

EUROPEAN RESEARCH OFFICE

United States Army

London, W.1, England

Grant Number DAERO-74-9019

THAMES POLYTECHNIC

A021691

AD

NEW POLYORGANOSILOXANES PREPARED FROM SILICATE MINERALS

Final Technical Report

By

B.R. Currell

August 1977

EUROPEAN RESEARCH OFFICE

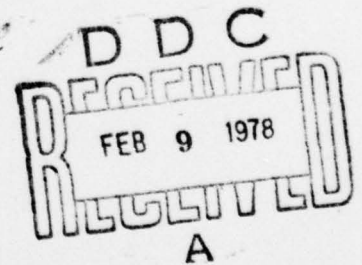United States Army

London, W.1, England

THAMES POLYTECHNIC

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) NEW POLYORGANOSILOXANES PREPARED FROM SILICATE MINERALS.		5. TYPE OF REPORT & PERIOD COVERED FINAL TECHNICAL REPORT MAR — AUG 77. 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) B. R. CURRELL		8. CONTRACT OR GRANT NUMBER(s) DAERO-74-G-019
9. PERFORMING ORGANIZATION NAME AND ADDRESS THAMES POLYTECHNIC LONDON UK		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6.11.02A 1T161102B32D 00-490
11. CONTROLLING OFFICE NAME AND ADDRESS U.S.A. R&S GROUP (EUR) BOX 65 FPO NEW YORK 09510		12. REPORT DATE AUG 77 13. NUMBER OF PAGES 50 p.
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE

DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, If different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silicones
Silicate Chemistry
Trimethylsilyation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

SEE OVER

391 763

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73

20 ABSTRACT

Several novel polyorganosiloxane systems have been prepared by the physical and chemical modification of inorganic polymers resulting from the trimethylsilylation of minerals such as biotite, muscovite, thuringite and wollastonite.

The extensive study of the trimethylsilylation step itself has given detailed information about the isomorphous replacement of silicon by aluminium in the silicate backbone, and the polymers produced by this step are interesting in themselves, showing marked stability to acid and base attack.

The modification of this initial or pre-polymer by a variety of physical and chemical techniques has led to a number of interesting systems:

1. thermal polymerisation gives high molecular weight products $\overline{M}_n$ ≈ 6000 approx.

2. reaction through pendant hydroxyl groups with

   $(CH_3)_3SiCl$, Ph_2PCl, $SOCl_2$, $(Ch_2=CH)(CH_3)SiCl_2$, $CH_2=CHSiCl_3$

   gives functionally substituted polyorganosiloxanes. (with molecular wt. of

3. reaction with $(CH_3)_2SiCl_2$ in the presence of hydrated ferric chloride gives products $\overline{M}_n$ ≈ 6000 containing labile chlorine atoms. approx.

Finally we have also investigated* the reactivity of the methyl groups $(CH_3)_3Si$ on the polyorganosiloxanes* and have already shown that they will react to give halogen precursors which can be used to give polyorganosiloxanes containing alcoholic and ester groupings.

* was investigated and it was shown that

CONTENTS

ABSTRACT

Several novel polyorganosiloxane systems have been prepared by the physical
and chemical modification of inorganic polymers resulting from the trimethyl-
silylation of minerals such as biotite, muscovite, thuringite and wollastonite.

The extensive study of the trimethylsilylation step itself has given detailed
information about the isomorphous replacement of silicon by aluminium in the
silicate backbone, and the polymers produced by this step are interesting in
themselves, showing marked stability to acid and base attack.

The modification of this initial or pre-polymer by a variety of physical and
chemical techniques has led to a number of interesting systems :

1.   thermal polymerisation gives high molecular weight products $\overline{M}_n \approx 6000$

2.   reaction through pendant hydroxyl groups with

      $(CH_3)_3SiCl$, Ph_2PCl, $SOCl_2$, $(CH_2=CH)(CH_3)SiCl_2$, $CH_2=CHSiCl_3$
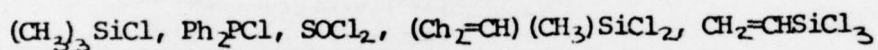
      gives functionally substituted polyorganosiloxanes.

3.   reaction with $(CH_3)_2SiCl_2$ in the presence of hydrated ferric chloride
      gives products $\overline{M}_n \approx 6000$ containing labile chlorine atoms.

Finally we have also investigated the reactivity of the methyl groups $(CH_3)_3Si$
on the polyorganosiloxanes and have already shown that they will react to
give halogen precursors which can be used to give polyorganosiloxanes containing
alcoholic and ester groupings.

1. INTRODUCTION

Prior to the commencement of this contract we had shown that the technique of trimethylsilylation developed by Lentz (1) which involves the conversion

$$\geqslant Si - O^- \longrightarrow \geqslant Si - O - Si(CH_3)_3$$
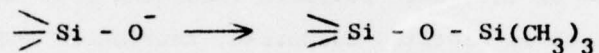
could be applied to a range of silicate minerals (2). We also knew that polyorganosiloxanes prepared by this method contained small but significant numbers of hydroxyl groups.

During the course of this contract we have determined the reactivity of these hydroxyl groups; investigated the control of their number in a polymeric species by heat treatment. We have also shown how the trimethylsilylation technique can be used to determine certain structural features of mica minerals.

However, in addition to completing these, our original objectives, we have prepared several completely novel polyorganosiloxane systems which contain functionally substituted fragments, and are illustrated by a schematic representation below:-

1.1 Thermal Polymerisation

$$XO - \left[\begin{array}{c} OX \\ | \\ Si - O \\ | \\ OX \end{array} \right]_3 - X \quad \xrightarrow[\text{30 hours}]{300^{\circ}C} \quad XO - \left[\begin{array}{c} OX \\ | \\ Si - O \\ | \\ OX \end{array} \right]_{27} - X \quad + \quad XOX$$

$$X = Si(CH_3)_3$$

<u>1.2 Hydroxyl addition</u>

(i) $ROH + (CH_3)_3SiCl \longrightarrow ROSi(CH_3)_3 + HCl$

(ii) $ROH + CH_3(CH_2=CH)SiCl_2 \longrightarrow$ $ROSiOR + HCl$, with CH_3 above and $CH=CH_2$ below the Si

(iii) $ROH + Ph_2PCl \longrightarrow ROPPh_2 + HCl$

$$R = XO - \left[\begin{matrix} OX \\ | \\ Si \\ | \\ OX \end{matrix} \right]_n$$

(iv) $ROH + CH_2=CHSiCl_3 \longrightarrow ROSi - CH = CH_2 + HCl$ with Cl above and below Si
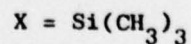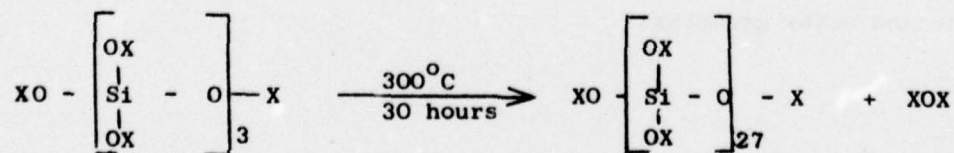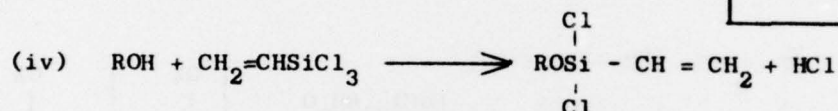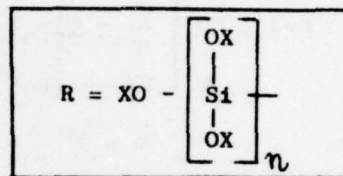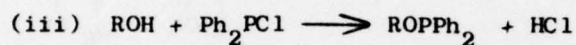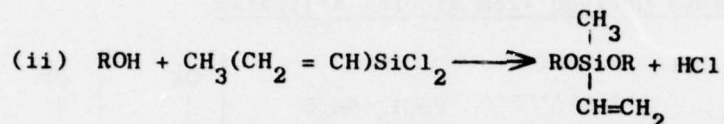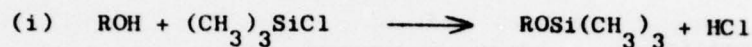
<u>1.3 Stability to acid/base redistribution</u>

$$ROH \xrightarrow[200^{\circ}C,\ 2.5\ hours]{H_2SO_4} ROH$$

$\bar{M}_n = 890$ \qquad $\bar{M}_n = 968$
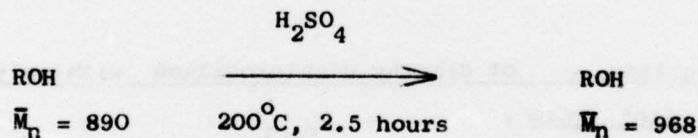
<u>1.4 Trimethylsilylation using polydimethylsiloxanes as the silylating agent</u>

This reaction gives products of the type shown below:

$$(CH_3)_3Si- \left[\begin{matrix} CH_3 \\ | \\ O - Si - O \\ | \\ CH_3 \end{matrix} \right]_x \left[\begin{matrix} OX \\ | \\ Si - O \\ | \\ OX \end{matrix} \right]_y X \xrightarrow{heat} \boxed{\text{high molecular weight polymers}}$$
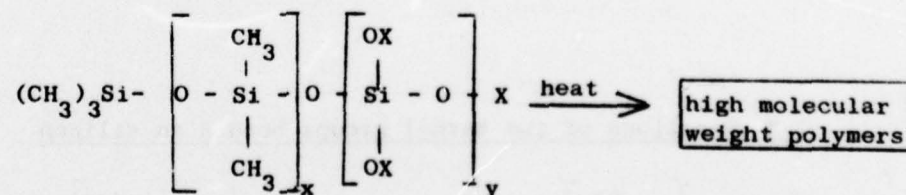
1.5 Catalytic reaction of dimethyldichlorosilane with polyorganosiloxanes derived from mineral silicates.

(a)

$$HO \begin{bmatrix} OX \\ | \\ Si - O \\ | \\ OX \end{bmatrix}_n - X \; + \; (CH_3)_2SiCl_2 \; \xrightarrow[\text{heat}]{FeCl_3 \cdot 6H_2O} \; XO \begin{bmatrix} OX \\ | \\ Si - O \\ | \\ OX \end{bmatrix}_6 \begin{matrix} OX \\ | \\ Si - O \\ | \\ OY \end{matrix} \begin{matrix} OX \\ | \\ Si - OX \\ | \\ OX \end{matrix}$$

n = 3

$Y = Si(CH_3)_2Cl$

(b)

$$HO \begin{bmatrix} OX \\ | \\ Si - O \\ | \\ OX \end{bmatrix}_3 - X \; + \; \begin{matrix} (CH_3)_2SiCl_2 \\ \text{(large excess)} \end{matrix} \; \xrightarrow[\text{heat}]{FeCl_3 \cdot 6H_2O} \; XO \begin{bmatrix} OX \\ | \\ Si - O \\ | \\ OX \end{bmatrix}_3 O \begin{matrix} OX \\ | \\ Si - OX \\ | \\ OX \end{matrix}$$
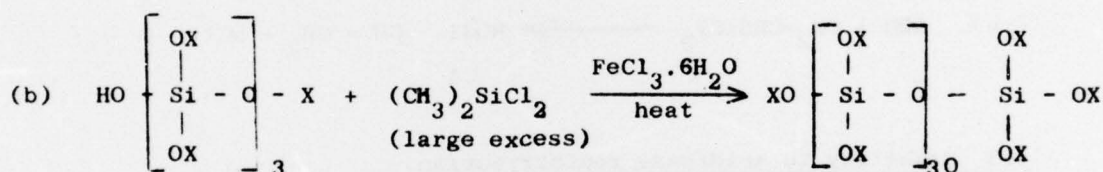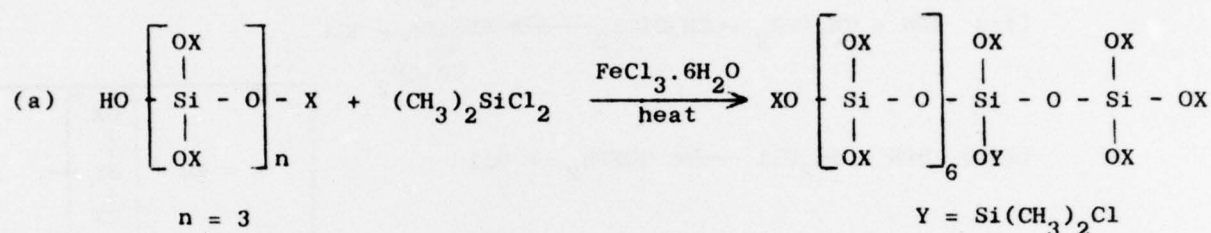
1.6 Catalytic reaction of dimethyldichlorosilane with polyorganosiloxanes and octamethyltetrasiloxane.

$$HO \begin{bmatrix} OX \\ | \\ Si - O \\ | \\ OX \end{bmatrix}_3 - X \; + \; (CH_3)_2SiCl_2 \; + \; \left[(CH_3)_2SiO\right]_4 \; \xrightarrow[\text{heat}]{\begin{matrix} FeCl_3 \cdot \\ 6H_2O \end{matrix}} \; XO - Si \begin{bmatrix} OX \\ | \\ Si \\ | \\ OX \end{bmatrix}_n O \begin{bmatrix} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{bmatrix}_m \begin{bmatrix} OY \\ | \\ Si - OX \\ | \\ OY \end{bmatrix}_p$$
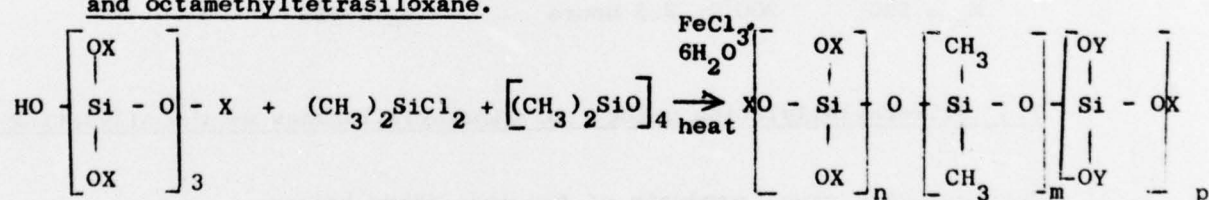
1.7 Reactions of the Methyl groups bonded to silicon

(i)

$$X \begin{bmatrix} OX \\ | \\ O - Si \\ | \\ OX \end{bmatrix}_3 OX \; + \; Cl_2 \; \xrightarrow[\text{4 hours}]{\text{W light}} \; T \begin{bmatrix} OT \\ | \\ O - Si \\ | \\ OT \end{bmatrix}_3 OT$$

$T = Si(CH_3)_2CH_2Cl$

(ii)

$$XO - \overset{\displaystyle OX}{\underset{\displaystyle OX}{\overset{|}{\underset{|}{Si}}}} - OX \bigg]_3 + Br_2 \xrightarrow[\text{4 hours}]{\text{W light}} VO - \overset{\displaystyle OV}{\underset{\displaystyle OV}{\overset{|}{\underset{|}{Si}}}} - OV \bigg]_3 \qquad V = Si(CH_3)_2CH_2Br$$

(iii)

$$\text{Polymer} - \overset{|}{\underset{|}{Si}} - \overset{|}{\underset{|}{C}} - Cl \xrightarrow[\text{HOAc 24 hours}]{\text{KOAc}} \text{Polymer} - \overset{|}{\underset{|}{Si}} - \overset{|}{\underset{|}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_3$$

$$\Bigg\downarrow \begin{array}{c} \text{dry} \\ HCl / CH_3OH \end{array} 96 \text{ hours}$$

$$\text{Polymer} - \overset{|}{\underset{|}{Si}} - \overset{|}{\underset{|}{C}} - O - \overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{Si}}}} - Vi \xleftarrow[\text{4 hours}]{\begin{array}{c} Cl_3ViSi \\ CCl_4 \end{array}} \text{Polymer} - \overset{|}{\underset{|}{Si}} - \overset{|}{\underset{|}{C}} - OH$$

$$Vi = (CH = CH_2)$$
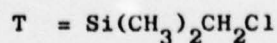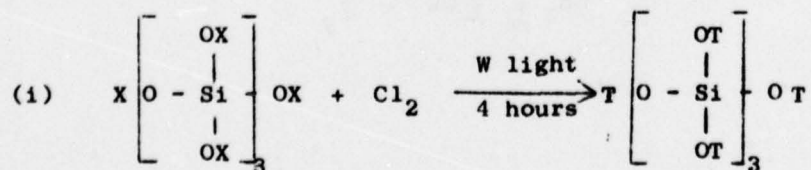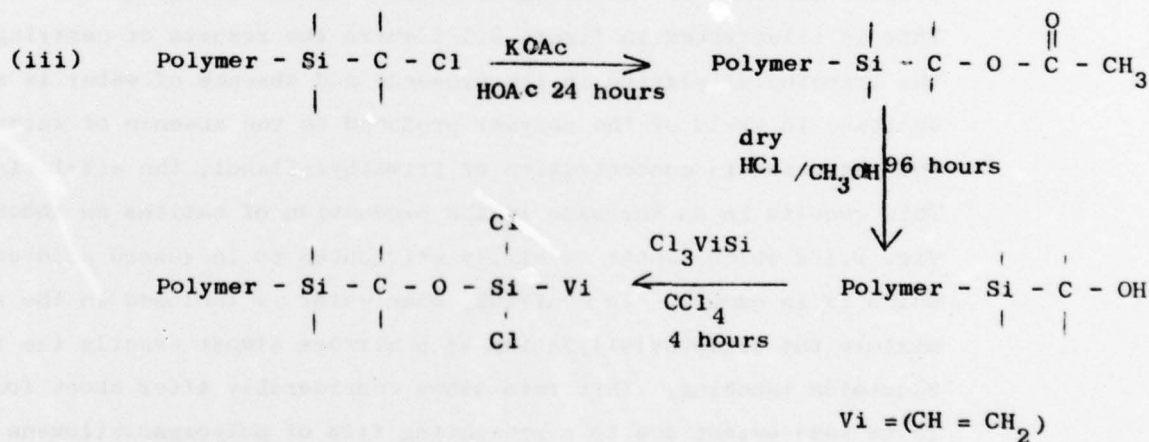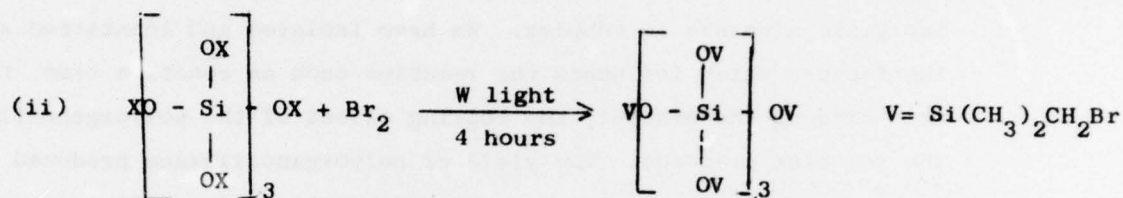
2. DISCUSSION

2.1   The trimethylsilylation reaction

2.1.1   The structure of the mineral

There is no doubt that the mechanism of the trimethylsilylation of
inorganic minerals is complex. We have isolated and identified some of
the factors which influence the reaction such as reaction time, the
mesh size of the mineral, the coating effect of the polyorganosiloxane a
the reaction proceeds. The yield of polyorganosiloxane produced increas
with decrease in mesh size for a fixed reaction time. If the sample of
mineral used contains a variety of mesh sizes the smaller particles
react first together with the outside of the larger particles. As a resu
the unreacted mineral consists of a homogenous mesh size. Careful exami
of the unreacted mineral revealed no marked differences to the starting
mineral except for a very slight opening of the cationic layers.

During the course of the reaction the production of the trimethylsilylat
product inhibits the leaching of cations by the acidic reaction media.
This is illustrated in figure 2.1/1 where the results of carrying out
the trimethylsilylation in the presence and absence of water is shown.
decrease in yield of the polymer produced in the absence of water is cau
the reduction in concentration of trimethylsilanol, the silylating agent
This results in an increase in the production of cations as shown in
fig. 2.1/2 which cannot be simply attributed to increased acid concentra
which is in excess. In contrast, when water is included in the reactior
mixture the trimethylsilylation step mirrors almost exactly the rate of
aluminium leaching. This rate slows considerably after about four hours
is to some extent due to a protecting film of polyorganosiloxane on the
mineral particles.
This is also illustrated in table 3/3 where the amounts of aluminium, ir
and magnesium leached in four sequential five hour reactions was greater
than a twenty hour continuous reaction. The importance of aluminium in
the backbone of the mineral as a chain breaking point has been discussed
previously (2) and we have also shown this by the trimethylsilylation
of some calcium aluminosilicate glasses (see table 3/6).(3)

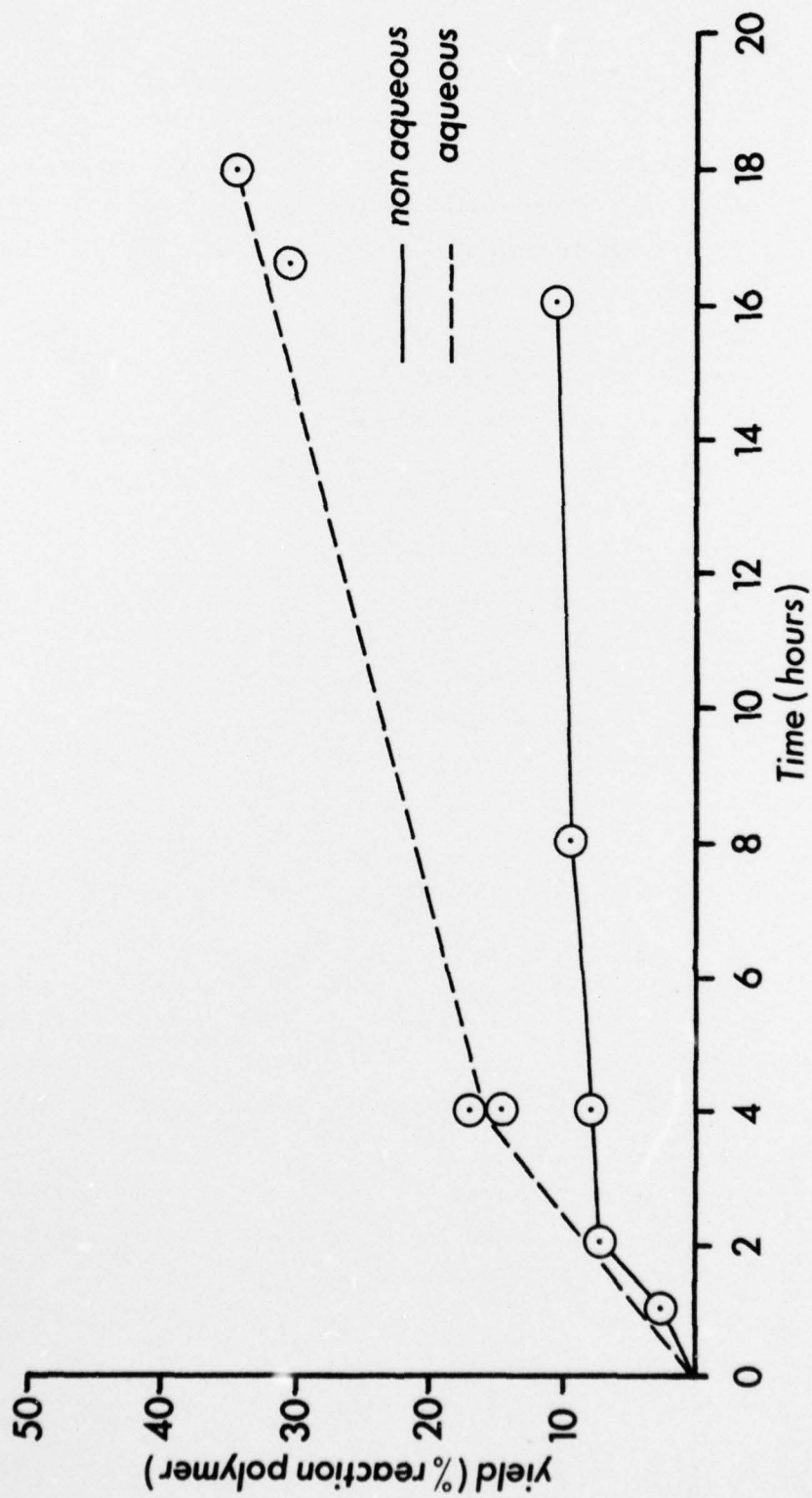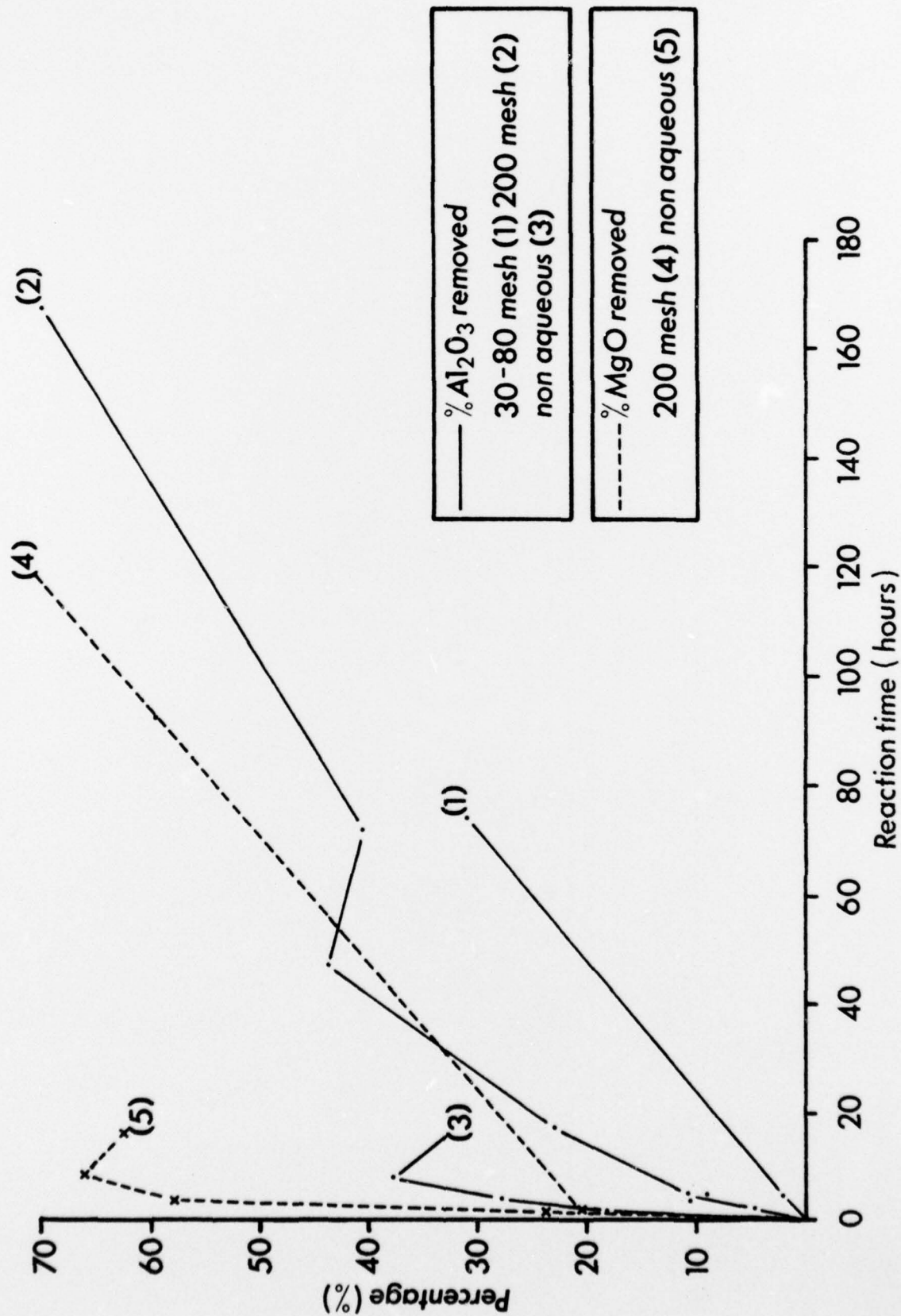Fig 2.1/1 Variation of mineral reaction in the presence and absence of water

Fig 2.1/2 The removal of magnesium and aluminium

% Al_2O_3 removed
30-80 mesh (1) 200 mesh (2) non aqueous (3)

% MgO removed
200 mesh (4) non aqueous (5)

Percentage (%)

Reaction time (hours)

It would appear that the production of large amounts of tetrakistrimethyl-
siloxysilane (I), and hexakistrimethylsiloxydisiloxane (II) is caused by
two factors; firstly, the aluminium appears to exist in domains which
gives a bimodal distribution of polyorganosiloxanes and secondly, the low
molecular weight siloxanes are in equilibrium with each other and with
high molecular weight fragments which breakdown to give (I).

2.1.2   Miscellaneous trimethylsilylation reactions

We have shown that hexamethyldisiloxane can be replaced by linear
polydimethylsiloxanes to give higher molecular weight products. The
proposed mechanism for the trimethylsilylation action of hexamethyldisiloxane
involves the production of trimethylsilanol and a similar reaction scheme is
proposed here to give mixed polyorganosiloxane and polydimethylsiloxane
polymers. These resinous gums show similar characteristics to the pure
polyorganosiloxanes produced in the standard trimethylsilylation reaction .

2.2 The physical modification of the polyorganosiloxanes prepared by the
trimethylsilylation reaction.

We have shown previously that the trimethylsilylation of the mineral
biotite results in a polyorganosiloxane of $\bar{M}_n \approx 890$ which consists of 47%
tetrakistrimethylsiloxysilane (I), 6% hexakistrimethylsiloxydisiloxane (II)
and 47% of higher molecular weight homologues. We have also suggested
that heating this material up to $\approx 150\,^{\circ}C$ increases its molecular weight
by the physical removal of I and II rather than a polymerisation reaction.
The condensation of hydroxyl groups does however aid the production of
higher molecular weight species on heating above $180\,^{\circ}C$. To test this
hypothesis heat treated biotite polymer ($180\,^{\circ}C$, 760 mmHg) in air for
two hours was completely trimethylsilylated by reacting the polymer
with trimethylchlorosilane. The hydroxyl bands present in the spectrum
before reaction were absent afterwards.   This fully trimethylsilylated
product was then heated at $300\,^{\circ}C$ for 5 hours in a flow of nitrogen gas
(the product would have lost hydrocarbon at this temperature in air).
The results were interesting in so far that a weight loss of 30.6% did
occur, the $\bar{M}_n$ increased to 5000; thus although the condensation of
hydroxyl groups may occur to produce high molecular weight species, other
polymerisation depolymerisation mechanisms are also occurring. We set
out to investigate the polymerisation mechanism by the following methods;
the use of gas flows rather than gas atmospheres; the effect of nitrogen
gas instead of air; and increased reaction times.

The effect of heating the biotite polymer in a flow of air rather than simply in an atmosphere of air results in an increased weight loss. At 100 $^{\circ}$C for 5 hours at atmospheric pressure the weight loss (2.5%) is only a fraction of the weight loss (50%) when the volatile components are swept away in an air current. The respective $\bar{M}n$'s obtained by these methods were 901 and 2453. The effect of the air flow is to encourage polymerisation, the forward reaction in the scheme shown below, by disturbing the equilibrium to the right by removal of low molecular weight components.

$$XO - \underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - O - \left[\underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - O\; X\right]_3 \xrightarrow[\text{5 hours}]{300\,^{\circ}C} XO - \underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - \left[O - \underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - O\; X\right]_{10} + XO - \underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - OX$$
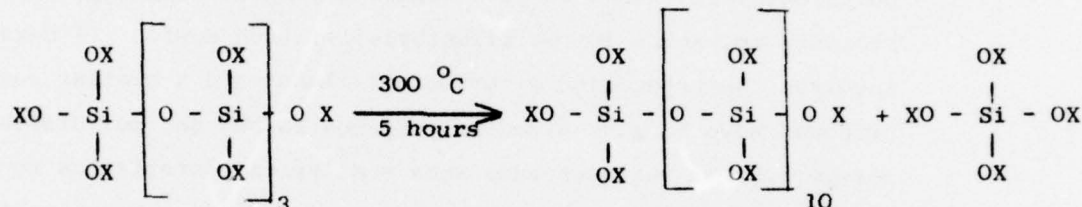
It seemed likely that heat treatment in a flow of nitrogen would give us high molecular weight materials which would remain soluble in organic solvents because the hydrocarbon content of the polymer would remain in situ.

We knew that heating the original polyorganosiloxane in air (300 $^{\circ}$C, 760 mmHg) gave an insoluble product. However, these same conditions in a nitrogen flow gave a product soluble in organic solvents with $\bar{M}_n \approx 4110$, this polymerisation was still being accompanied by weight losses of about $\sim$ 60%. It was interesting that the weight loss remained at this figure when the heating time was increased to 30 hours and even more encouraging to obtain a resinous material soluble in organic solvents with $\bar{M}_n \approx 7000$. At this stage the original polymerisation depolymerisation mechanism has changed to a different mechanism. Increasing the reaction time to sixty hours only increased the weight loss by a further 6%, the hydrocarbon content decreased to 27% which gave an insoluble product.

Fig 2.2/1 Variation of weight loss with temperature

Legend:
- ⊙ 760 mm Hg
- ⊡ 3 mm Hg
- △ 760 mm Hg [N₂]
- ◇ Preheated

Weight loss (%) vs Temp °C
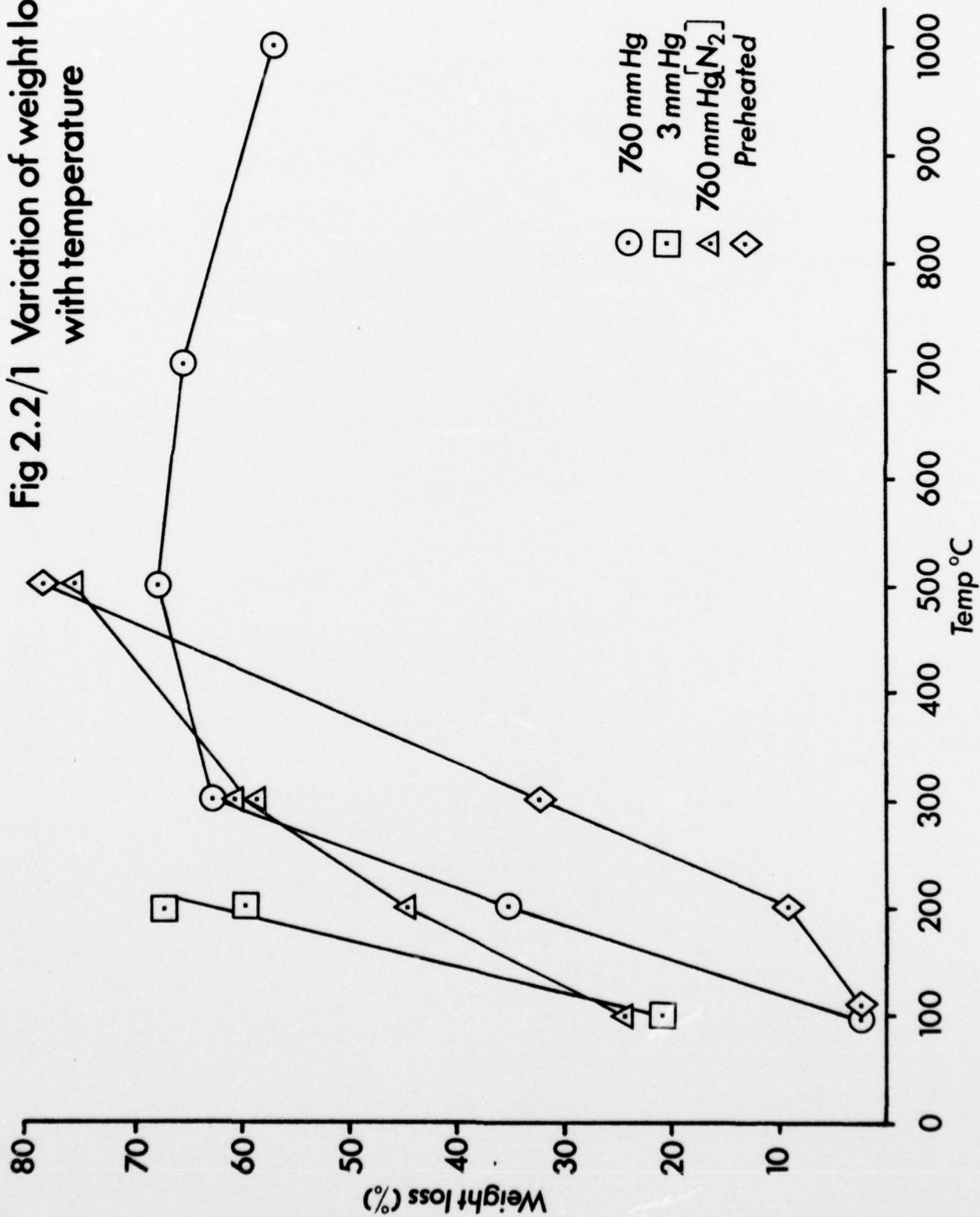
Fig 2.2/2 The variation of $\bar{M}n$ vs weight loss on heating under specified conditions
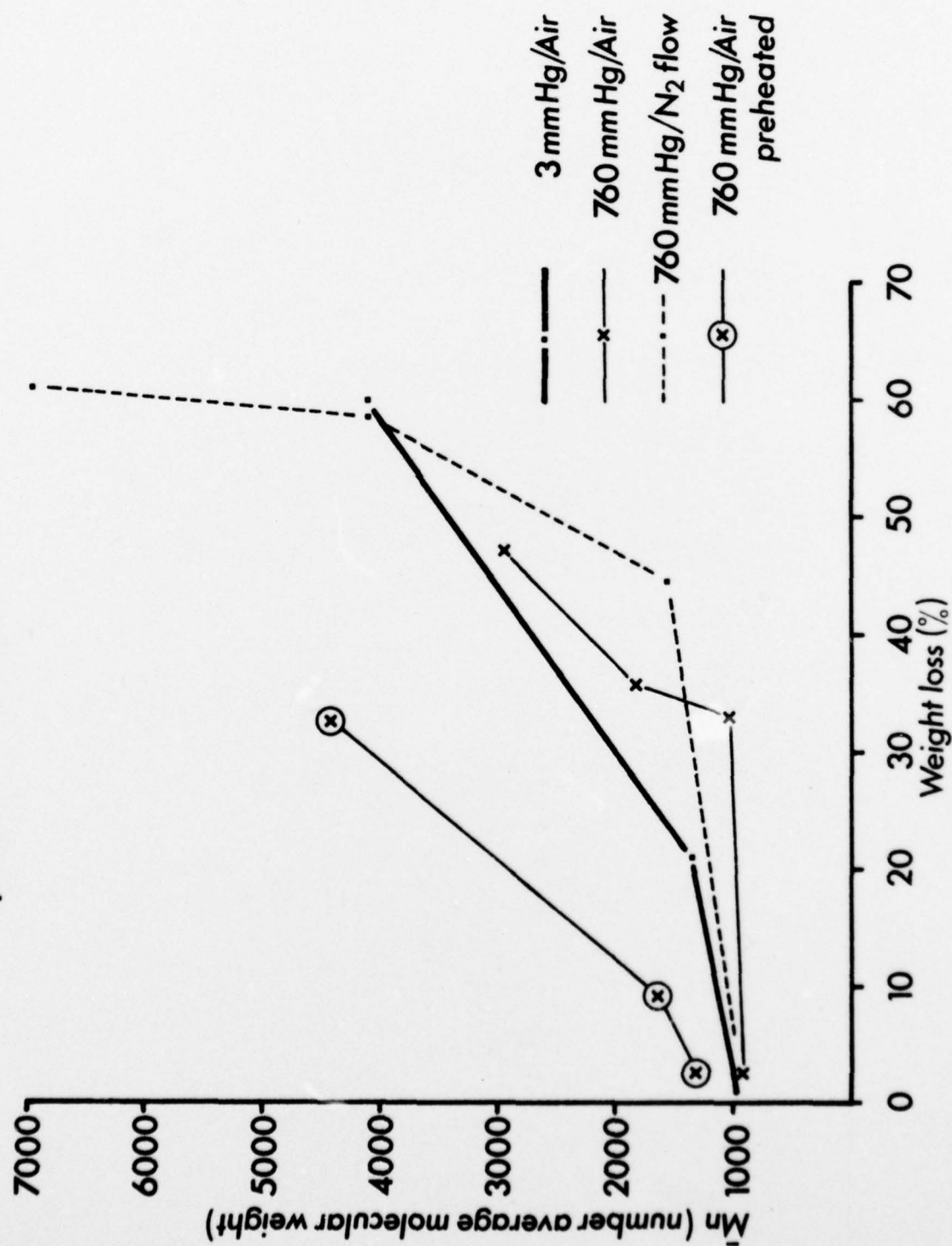
A further interesting development has been to use pre-heat treated materials for our thermal polymerisation. The effect of removing I and II at low temperatures, that is without affecting the high molecular weight end of the bimodal distribution results in a more thermally stable product - see Fig. 2.2/1. However although a substantial portion of I and II had been removed before the second heat treatment, I and II were still being produced. We set out to investigate this phenomenon by attempting to distil the polyorganosiloxane and examine the volatile products.

In the initial stages the removal of I and II dominates to give hydroxylated products of $\overline{M}_n \approx 1500$. Further treatment produces more I and II with an increase in $\overline{M}_n$ caused to some extent by the condensation of hydroxyl groups but more important is the depolymerisation-polymerisation sequences.

$$
\begin{array}{ccc}
\text{OX} & \text{OX} \quad \text{OX} & \\
| & | \quad\quad | & \text{high molecular} \\
\text{XO} - \text{Si} - \text{OX} \rightleftharpoons & \text{XO} - \text{Si} - \text{O} - \text{Si} - \text{OX} \rightleftharpoons & \text{weight products} \quad +\text{XOX} \\
| & | \quad\quad | & \\
\text{OX} & \text{OX} \quad \text{OX} & \\
(\text{I}) & (\text{II}) &
\end{array}
$$
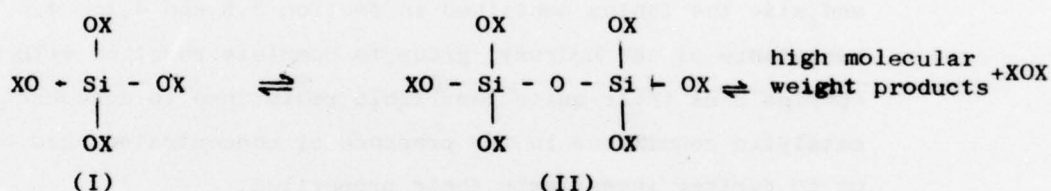
The production of I and II was further illustrated by distilling biotite polymer (47% Si_1, 6% Si_2) and analysing the residue and distillate.

Treatment	Si_1	Si_2	HMD	$\overline{M}_n$
Residue/distillate	%	%		
300 °C, 5 hours residue	70.5	4.9	-	1450
300 °C, 5 hours distillate	204.8	2.7	present	-
450 °C residue	0.4	1.0	-	4125
450 °C distillate	50.3	0.0	present	-

HMD = hexamethyldisiloxane

This suggests that the polymerisation depolymerisation mechanism which is well known with polydimethylsiloxanes is occurring here.

The products of these heating experiments are air stable and show a variety of physical characteristics. We have started to investigate their flash cooling to give glass like materials.

The thermal stability of these materials compare very favourably with polydimethylsiloxanes and their increased resistance to acid/base redistribution makes them very useful.

2.3. The reaction of hydroxyl groups and redistribution reactions.

We have previously reported that reactions as shown below do occur, (3).

$$\geqslant Si-OH \ + \ (CH_3)_3SiCl \ \longrightarrow \ \geqslant Si-O-Si(CH_3)_3$$

$$\geqslant Si-OH \ + \ Ph_2PCl \ \longrightarrow \ \geqslant Si-O-SiPPh_2$$

$$\geqslant Si-OH \ + \ CH_2=CHSi(CH_3)Cl_2 \longrightarrow \geqslant Si-O-\underset{\underset{Cl}{|}}{Si}(CH_3)CH=CH_2$$
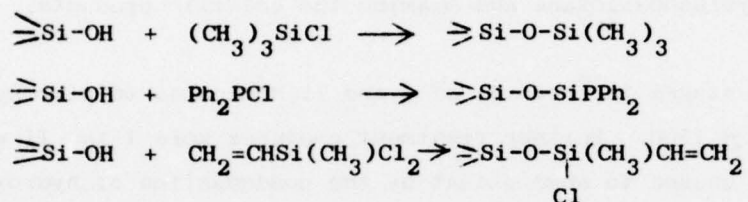
and see also the tables contained in section 3.5 and 4.1 - 4.6. However the resistance of the hydroxyl group to complete reaction with chlorinated species plus their quite remarkable resistance to condensation under catalytic conditions in the presence of concentrated acid or base has lead us to further investigate their properties.

Table 2/1   Condensation reactions of polyorganosiloxanes

Reactants	Reaction Temp ($^{\circ}$C)	Conditions Time	Catalyst	$\overline{M}_n$ (found)
III + IV	140	2.5 hours	KOH	560
III + IV	200	2.5 hours	KOH	520
III + IV	140	2.5 hours	H_2SO_4	604
III	0-12	10 days	H_2SO_4	958
III	200	2.5 hours	H_2SO_4	968
III	200	2.5 hours	KOH	883

III   Polyorganosiloxane $\overline{M}_n$ 890   IV   Octamethyltetrasiloxane

Birchall (4) has reported the stability of silane triols when coupled to ethylene oxide units in compounds such as $CH_3O(CH_2CH_2O)_3CH_2CH_2CH_2Si(OH)_3$ and they have proposed configurations such that the hydroxyl hydrogen is coupled, by hydrogen bonding to the oxygen atoms of the ethylene oxide units. Similarly in our higher molecular weight polyorganosiloxane units

$$(CH_3)_3Si — O \left[\begin{array}{c} Si(CH_3)_3 \\ | \\ O \\ | \\ Si — O \\ | \\ O \\ | \\ Si(CH_3) \end{array} \right]_n Si(CH_3)_3$$

$$n = 3-14$$
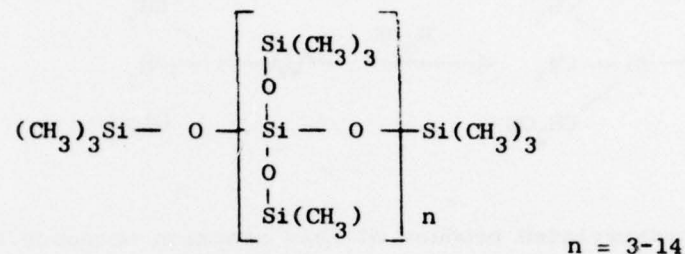
the hydroxyl moieties are found in a network of oxygen atoms formed by the siloxane bridges. The infrared spectrum of the polyorganosiloxane showed a broad band at 3000-3500 cm^{-1} indicative of a strongly hydrogen bonded species. After reactions involving various chlorinated species the products still showed signs of the hydroxyl group, and we would postulate that the reactivity of the specific hydroxyl groups depend upon its exact environment in the polymer chain.

We have now shown that if the hydroxyl group is separated from the polyorganosiloxane chain by a carbon chain, reaction occurs quantitatively with vinyltrichlorosilane (CH_2=$CHSiCl_3$) whereas with the unmodified polyorganosiloxane vinyltrichlorosilane will not react significantly even at elevated temperatures. The first stage in the reaction sequence was to prepare a hydroxyl group bound through carbon to the polyorganosiloxane. Thus the polymer derived from wollastonite (C, 31.5, H, 8.3, $\overline{M}_n$ = 890) was treated with chlorine gas in the presence of a tunsten lamp to give a product containing chlorine (Cl, 30.5%, $\overline{M}_n$=1166). This product was converted to an acetate derivative which was subsequently reacted with methanol to give a methanolic type species. This reaction sequence can be represented as follows (see also section 2.5).

$$XO - \begin{bmatrix} OX \\ | \\ Si - OX \\ | \\ OX \end{bmatrix}_n \xrightarrow{Cl_2} -\!\!\!\wedge\!\!\!\wedge\!\!\!- Si \begin{matrix} -CH_3 \\ -CH_3 \\ -CH_2Cl \end{matrix}$$

$$\downarrow KOAc$$

$$-\!\!\!\wedge\!\!\!\wedge\!\!\!- Si \begin{matrix} -CH_3 \\ -CH_3 \\ -CH_2OH \end{matrix} \xleftarrow{CH_3OH} -\!\!\!\wedge\!\!\!\wedge\!\!\!- Si \begin{matrix} -CH_3 \\ -CH_3 \\ -OAc \end{matrix}$$
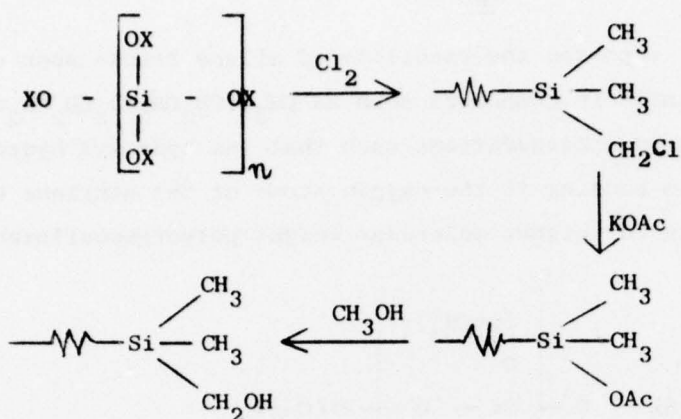
The hydroxylated product of this reaction sequence reacts quantitatively with vinyltrichlorosilane to give a reddish brown elastomeric product. The infrared spectrum of the hydroxyl precursor shows evidence for both free and bonded hydroxyl groups, the reaction product whilst still showing evidence for the bound hydroxyl (has no signal for the free hydroxyl) - and signals for the C=C absorbtion and $=C\!\!<^H$ stretching frequency.

Although species such as thionylchloride do not react directly with the hydroxyl group in large numbers, they do react by chain breaking and subsequent addition. The nature of the thermal polymerisation mechanism together with the reactions of species such as thionylchloride and phenylisocyanate leads us to suggest that materials will result from heating these materials together at higher temperatures. However we have pursued two other routes in priority during the last six months of the contract and these are in sections 2.4 and 2.5.

2.4. The catalytic reaction of polyorganosiloxanes with dimethyl-dichlorosilane.

The polymerisation of dimethyldichlorosilane with diethoxydimethylsilane is well known (5); we decided to attempt to extend the scope of this reaction by replacing the alkoxyalkylsilane with a polyorganosiloxane polymer in the reaction scheme.

The reaction of dimethyldichlorosilane with the polyorganosiloxane derived from wollastonite does give some reaction by elimination of hydrogen chloride.

$$\overset{OX}{\underset{OX}{-\!\!\text{\scriptsize WW}\!\!- Si}} - O - \overset{CH_3}{\underset{CH_3}{Si}} - OH \;+\; Cl - \overset{Cl}{\underset{CH_3}{Si}} - CH_3 \;\Longrightarrow\; \overset{OX}{\underset{OX}{-\!\!\text{\scriptsize WW}\!\!- Si}} - O - \overset{CH_3}{\underset{CH_3}{Si}} - O - \overset{Cl}{\underset{CH_3}{Si}} - CH_3$$
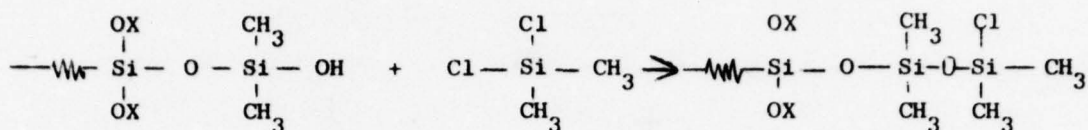
However as we showed in section 2.3, this reaction depends on the environment of the hydroxyl groups.

The results of the reaction of dimethyldichlorosilane with polyorganosiloxanes in the presence of a catalyst ($FeCl_3.6H_2O$) are shown in table 2.2. As the ratio of dimethyldichlorosilane to polyorganosiloxane increases the $\overline{M}_n$ increases until the product becomes insoluble. When the ratio of reactants is 1:1 the polymer has a chlorine content (13%) which is capable of further reaction with methanol, butanol and pentan-1,5-diol. The highest molecular weight species so far obtained $M_n \approx 5000$ also contains a small amount of chlorine.

The volatile components isolated from these reactions show that up to 0.5 reactant ratio, all the dimethyldichlorosilane has been converted to trimethylchlorosilane and above this ratio some of the dimethylchlorosilane is unreacted. A small amount of hexamethyldisiloxane is also produced during the course of the reaction. The absence of chlorine in the product leads us to suggest the following reaction pathway

$$XO - \left[\overset{OX}{\underset{OX}{Si}}O - \overset{OX}{\underset{OX}{Si}}\right]_2 OX \;+\; (CH_3)_2SiCl_2 \;\xrightarrow{FeCl_3.6H_2O}\; XO\left[\overset{OX}{\underset{OX}{Si}} - O - \overset{OX}{\underset{OX}{Si}}\right]_2 OY \;+\; (CH_3)_3SiCl$$

in situ

$$Y = Si(CH_3)_2Cl$$

$$YO - \overset{OX}{\underset{OX}{Si}} - O\left[\overset{OX}{\underset{OX}{Si}} - OX\right]_2 \;+\; XO - \overset{OX}{\underset{OX}{Si}} - O - \left[\overset{OX}{\underset{OX}{Si}} - O\right]_2 X \;\xrightarrow{FeCl_3 6H_2O}\; X - O\left[\overset{OX}{\underset{OX}{Si}} - O\right] - \overset{OX}{\underset{OX}{Si}} - OX \right]_n \quad n > 4$$
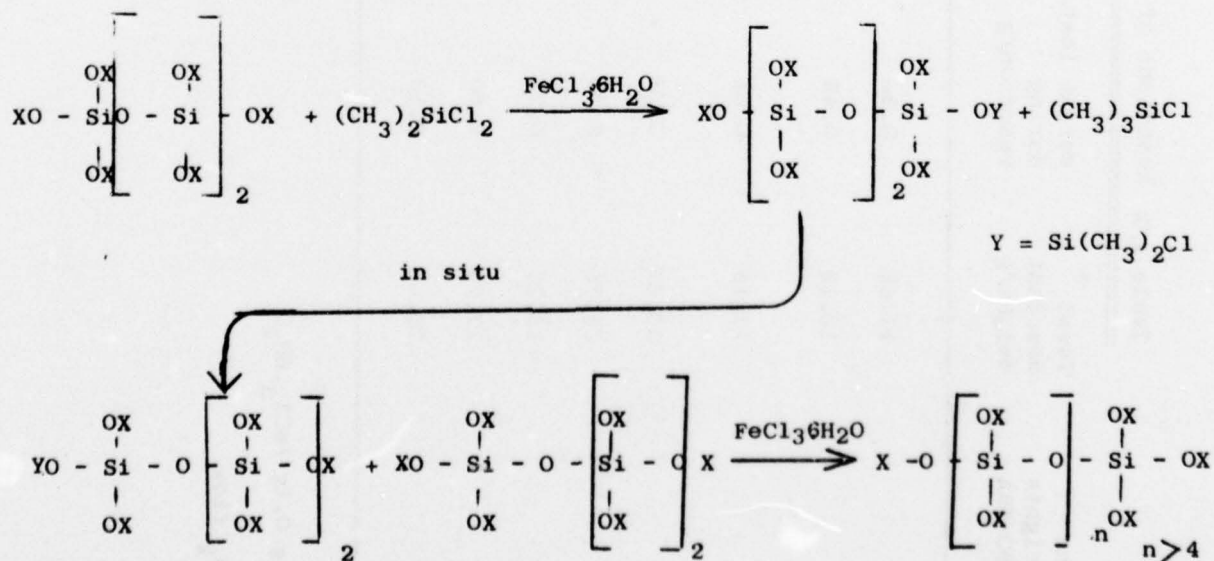
Table 2/2   Reactions of polyorganosiloxanes and Me_2SiCl_2 with catalyst

Ratio of the reactant weights Me_2SiCl_2/890-PRA	Total Reactant Weight/g *	Weight lost during reaction/g	Weight of Volatiles Collected/g	Weight of Residue/g	Nature of Product	$\overline{Mn}$
0.12	11.45	0.36	0.89	9.90	Fluid	1200
0.20	12.16	0.48	2.05	9.33	Viscous Fluid	1520
0.30	13.15	0.57	3.62	8.74	Viscous Gum	2580
0.34	13.66	2.58	2.41	8.79	Viscous Gum	5100' †
0.40	14.15	0.73	4.91	8.29	Insoluble Solid	
0.51	15.20	0.76	4.92	8.97	Insoluble Solid	
0.70	17.34	1.60	7.29	8.00	Insoluble Solid	
1.00	20.16	0.69	10.15	8.77	Insoluble Solid	

* including 0.1g $FeCl_3.6H_2O$

† under N_2 flow

Fig 2.4/1 Variation of $\bar{M}$n number average molecular weight with reactant ratio

Weight of reactants $\left(\dfrac{Me_2SiCl_2}{890-PRA}\right)\dfrac{g}{g}$
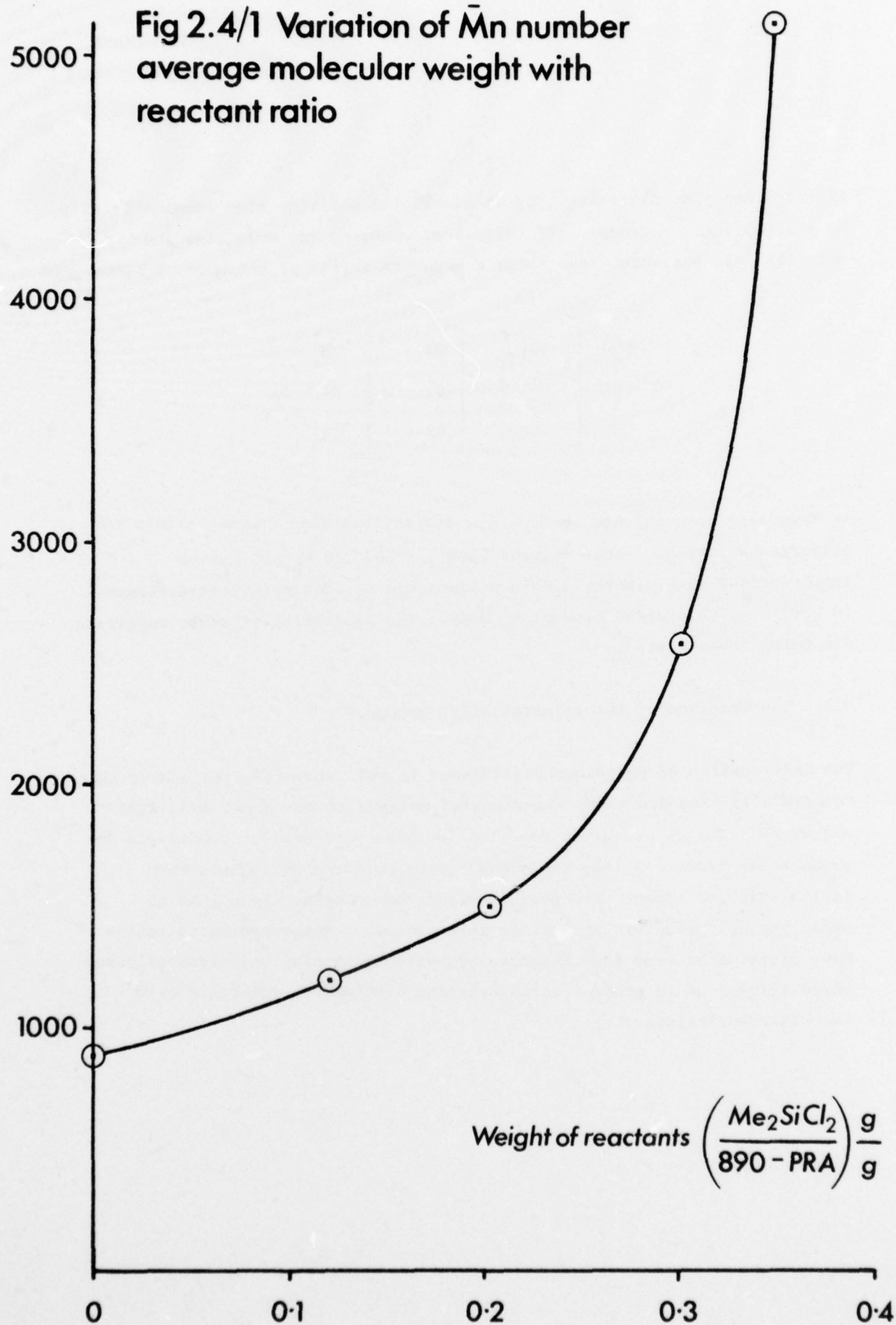
If the dimethyldichlorosilane is in excess the chlorine atom remains in situ as a $Si(CH_3)_2Cl$ group. If instead of removing the volatiles the materials are extracted into water a separate series of polymers $M_n \simeq 2000\text{-}3000$.

$$XO - \underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - \left[O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} \right]_n O \left[\underset{\underset{OX}{|}}{\overset{\overset{OX}{|}}{Si}} - O \right]_m \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - OX$$
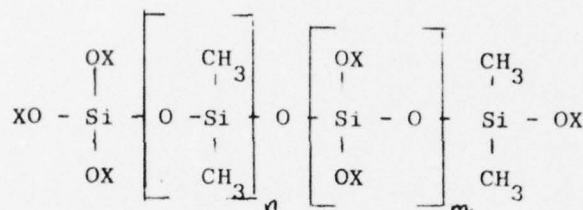
We have also been able to incorporate dimethylsiloxane fragments into the polyorganosiloxanes - thus olivine (50% I + 50% II) $\overline{M}_n$ 490 can be copolymerised with dimethyldichlorosilane and D_4 (octamethyltetrasiloxane) to give a soluble mixed product $\overline{M}_n$ 3240. The properties of these materials are being investigated.

2.5   The reaction of the trimethylsilyl groups.

The chlorination of polydimethylsiloxanes is well known (6,7,8) and we have successfully extended these experimental methods to our novel polyorgano- siloxanes. The chlorination reaction (we have used similar conditions to produce the bromo and iodo compounds) gives polyorganosiloxanes with labile chlorine atoms. We have converted the chloride group into an hydroxymethyl group via an acetoxy intermediate. These synthetic routes have given us an even more reactive hydroxyl containing polyorganosiloxane which allowed us to produce an interesting elastomer by reaction with trichlorovinylsilane.

It appears that the hydroxyl group attached to the siloxane chain via
a methylene group is much less hydrogen bonded than in the straightforward
silanol group. The synthetic route to this species:-

$$
\begin{array}{ccc}
OX & CH_3 & \\
| & | & \\
-\!\!\wedge\!\!\wedge\!\!\wedge\!\!- Si & - O - Si & - CH_2OH \\
| & | & \\
OX & CH_3 &
\end{array}
$$
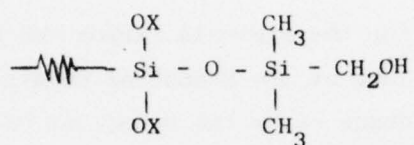
is very straightforward and the intermediates are interesting as precursors.

$$
\begin{array}{ccc}
OX & CH_3 & \\
| & | & \\
-\!\!\wedge\!\!\wedge\!\!\wedge\!\!- Si & - O - Si & - CH_2Z \\
| & | & \\
OX & CH_3 &
\end{array}
\qquad
\begin{array}{cccc}
OX & CH_3 & & O \\
| & | & & \| \\
-\!\!\wedge\!\!\wedge\!\!\wedge\!\!- Si & - O - Si & - O & - C - CH_3 \\
| & | & & \\
OX & CH_3 & &
\end{array}
$$
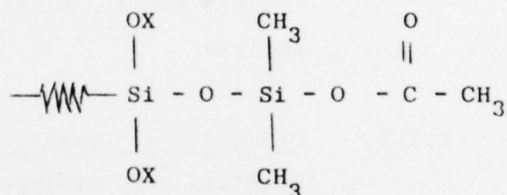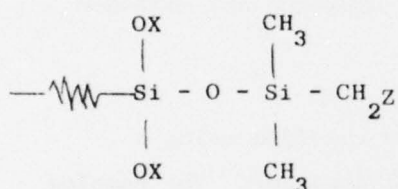
Z= Cl, Br, or I.

3. EXPERIMENTAL

3.1.1. <u>Microanalyses</u> for the elements carbon and hydrogen were carried out either at the School of Chemistry, Thames Polytechnic, London or by the School of Chemistry, Polytechnic of North London, Holloway Road, London. At Thames Polytechnic analyses were carried out using a Hewlett Packard Model 185 carbon, hydrogen and nitrogen analyser.

3.1.2. <u>Differential thermal analyses</u> were recorded using a Standata 6-25 Differential Thermal Analyser. The samples were heated in an atmosphere of air using alumina as a standard. The furnace was programmed to give a linear increase in temperature from ambient to 1000 $^\circ$C over a period of approximately 2 hours.

3.1.3. <u>Differential scanning calorimetry</u> was performed on certain products using a Perkin Elmer DSC-2. The instrument was programmed to give a temperature increase from 270 $^\circ$C to 773 $^\circ$C at a rate of 20 deg. C min^{-1}.

3.1.4. <u>Gel permeation chromatography</u> on the products was performed either at Thames Polytechnic or at the Rubber and Plastics Research Association of Great Britain (R.A.P.R.A.). The instrument used at Thames Polytechnic was a Waters Associates Model 501, High Performance Liquid Chromatograph comprising four μ-Styragel columns with permeability ranges 100 $\overset{\circ}{A}$, 500 $\overset{\circ}{A}$, 10^3 $\overset{\circ}{A}$ and 10^4 $\overset{\circ}{A}$, each having a plate count of greater than 3000. Peaks were detected in both cases using refractive index detectors and relative molecular weights assigned by calibrating the instruments with Waters Associates polystyrene and polyglycol standards. The eluting solvents used were chloroform at Thames Polytechnic and tetrahydrofuran and o-dichlorobenzene at R.A.P.R.A.

3.1.5.   A modified Zerewitinoff method was used to determine hydroxyl groups present on the polymers. The Grignard reagent was prepared by the method of Siggia (9) and the apparatus calibrated using phenol and β-naphthol.

3.1.6.   Thin layer chromatography. The products from the polyorganosiloxane derivatives (2μl) were dissolved in chloroform and applied to a glass plate coated with silica gel. The plate was run in a tank containing benzene/ethyl acetate and developed with iodine vapour. The method of Hoebbel (10) has been investigated as a further thin layer chromatography method.

3.1.7.   Infrared spectra were recorded using a Perkin Elmer Model 337 Grating Infrared Spectrophotometer over the wavelength range 4000 - 400 cm^{-1}. All greases and liquids were examined as capillary films between either potassium bromide or sodium chloride plates; starting and unreacted minerals from trimethylsilylation reactions were run as potassium bromide discs; and low melting solids were run by pressing between two potassium bromide plates, or by deposition from ether.

3.1.8.   Molecular weights were determined using a Knauer vapour pressure osmometer. The instrument was calibrated using solutions of benzil, polystyrene and polyglycols in chloroform.

3.1.9.   Gas Liquid Chromatographic analyses were carried out using a Pye Series 104 Gas Chromatograph. The methods of Gotz and Masson (11) and Lentz (1) were used to identify the compositions of reaction products from trimethylsilylation of mineral silicates.

3.1.10   Nuclear magnetic resonance spectra were recorded using a
Varian A-60A 60 MHz spectrophotometer. The instrument was
used exclusively for examining reaction products for the
presence of hydroxyl groups remaining on the siloxane backbone
of the polymers after the trimethylsilylation reaction.

3.1.11   X-ray powder diffraction. The photograph was taken on a
Enraf Nonius TN20 X-ray diffractometer using a copper target
and a nickel filter at 30KV, 18 mA. The 180 mm film was
exposed for 10 hours.

3.1.12   Atomic Absorption spectroscopy

This work was carried out on a Varian Techtron AA6 atomic
absorption spectrophotometer.

3.1.13   X-ray fluorescence

The mineral analysis was carried out on a Cambridge
Instrument Mk 9 microscan at 20 KV, 4.5×10^{-8} amps
specimen current, ZAF corrections applied.

3.2 Identification of the mineral.

The minerals were characterised by their X-ray diffraction patterns (12);
infrared spectra (13); and by differential thermal analysis (14).
The mineral phlogopite (Harty Mountain Range, Western Australia) was analysed
completely in our own laboratories and at the Department of Mineralogy,
British Natural History Museum, London. We have also used X-ray
fluorescence techniques for the elemental analysis of phlogopite, biotite
and olivine. The results are shown below in tables 3/1; 3/2.

Table 3/1

Mineral	Found (%)				
	Si	Al	Fe	Mg	Ca
Biotite	17.3	8.9	17.0	2.1	0.2
Thuringite	10.8	10.3	22.7	4.0	0.1

The major constituents of the minerals biotite and thuringite.

3.3   Trimethylsilylation reactions

3.3.1 The trimethylsilylation of mineral silicates using hexamethyldisiloxane.

In a typical reaction isopropyl alcohol (100 cm^3), hydrochloric acid
(d = 1.18; 50 cm^3) and hexamethyldisiloxane (66.6 cm^3) were added to the
silicate (10g, 200 or 300 mesh) which had been slurried with water (40 cm^3).
The mixture was stirred and heated for a specified time at a reflux temperature
of $72^{\circ}C$.   After the mixture had cooled it was centrifuged to give a
hexamethyldisiloxane layer, a water-isopropyl alcohol layer and a layer of
unreacted mineral. The organic layer was carefully isolated and excess
solvent removed by evaporation ($40 ^{\circ}C$, 17 mmHg) to yield a mixture of
polyorganosiloxanes. The product was dried to constant weight in a drying
pistol ($45 ^{\circ}C$, 3 mmHg). The unreacted material, after washing with water,
isopropyl alcohol and ether was dried to constant weight at an oven temperature
of $105 ^{\circ}C$.
The aqueous layer, hexamethyldisiloxane layer and the unreacted minerals were
then subjected to a battery of analytical procedures.

Table 3/2

	Phlogopite (wet)	Phlogopite (X-ray)	Biotite (X-ray)	Olivine (X-ray)
SiO_2	40.02	48.84	42.42	39.24
Al_2O_3	15.02	14.94	21.75	0.03
TiO_2	0.57	0.60	0.47	0.02
Fe_2O_3	0.99	} 0.60	} 27.07	} 10.93
FeO	2.03			
MnO	0.03	0.13	0.39	0.17
MgO	26.04	22.13	0.71	46.64
Rb_2O	0.04	-	-	-
Na_2O	0.20	0.09	0.15	0.02
CaO	0.41	0.00	0.00	0.01
K_2O	10.40	6.62	5.73	0.00
H_2O^+	2.66	} 1.51	} 1.24	
H_2O^-	0.02			
F	2.86	1.00	-	-

The complete analysis of phlogopite, biotite and olivine by wet chemical and X-ray methods.

The variation in polymer yield with sequential or continuous reactions.

Biotite (10g) was reacted for 20 hours continuously using the general method of trimethylsilylation. The weight of unreacted mineral and polymer formed were recorded.

A further quantity of mineral (10g) was reacted for 5 hours. The polymer was isolated and the unreacted mineral cleaned in the usual way. The unreacted mineral was placed in a fresh reaction mixture and reacted for a further 5 hours. This procedure was followed for two further 5 hour intervals so that the original mineral had been reacted for a total of 20 hours. The aqueous layers for the various reactions were also analysed to give the extent of leaching during the course of the trimethylsilylation reaction.

Table 3/3

Reaction time	% reaction	Analysis of aqueous media (ppm)		
		Al	Fe	Mg
5	8.25	163	243	10
10	9.17	130	185	8
15	9.15	130	185	8
20	9.29	118	179	7
20 (continuous)	19.20	415	616	28

A comparison of continuous and sequential trimethylsilylation reaction.

3.3.2   The variation in polymer yield with mesh size.

Phlogopite (1 g) was reacted with water (4 cm^3), isopropyl alcohol (10 cm^3), hydrochloric acid (5 cm^3, d 1.18) and hexamethyldisiloxane (66.6 cm^3) for four hours using the standard trimethylsilylation reaction conditions. The variation of mesh size with weight of polymer produced is shown in Table 3/4.

TABLE 3/4

Mineral	Mesh Size	Wt of polymer (g)	Wt. unreacted Mineral (g)	% reaction *
Phlogopite (1g)	200	0.1726	0.8674	18
Phlogopite (1g)	30-80	0.0378	0.9216	12

* Percentage reaction has been calculated on the basis of the weight of unreacted mineral.

Two samples of biotite (10g each, St. Dennis, Cornwall), were examined by the standard trimethylsilylation reaction. One sample of mineral (A) had the sieve analysis, 1.07% retained 30 mesh, 64.75% retained 80 mesh, 27.13% retained 200 mesh, 3.49% retained 300 mesh and 3.55% passed 300 mesh, the other sample (B) was ground to pass 300 mesh.   Sample A gave 2.36 g polymer and in the same time sample B gave 5.07 g of polymer

3.3.3   The rate of cation leaching during the course of the
        trimethylsilylation reaction.

A series of reactions have been carried out using a standard and modified trimethylsilylation technique. The experiments (**)were carried out without the addition of water in the reaction mixture. The results are tabulated in table 3/5.

3.3.4 The trimethylsilylation of some calcium aluminosilicate glasses

In a typical reaction a sample of a glass 191ALD (composition: SiO_2 36.9%; Al_2O_3 26.8%; CaO 36.3%) was trimethylsilylated using the previously described mixture of hydrochloric acid, isopropanol, hexamethyldisiloxane and water.

The polymeric product was isolated and analysed by g.l.c. to give the following percentages of tetrakistrimethylsiloxysilane, (I) hexakistrimethylsiloxydisiloxane (II), octakistrimethylsiloxytrisiloxane (III) and decakistrimethylsiloxytetrasiloxane (IV). (Found: I, 58.8%; II 26.9%; III, 13.4%; IV, 0.9%). The results for the other glasses are shown in table 3/6. We acknowledge the gift of four glass materials from Corning Glass.

TABLE 3/5

Wt of phlogopite (g)	Reaction Time (hrs)	Wt of Polymer (g)	Wt of unreact. (g)	% reaction	% Al_2O_3 removed	% MgO removed
4	1	-	3.66	8.3	4.6	23.6
2	1 **	0.05	1.87	6.6	10.1	20.4
2	2 **	0.14	1.83	8.7	18.4	
4	4	0.59	3.25	18.6	9.9	
1	4	0.17	0.86	13.2	10.6	
1	4 *	0.04	0.92	7.9	2.3	
2	4 **	0.15	1.85	7.4	28.2	58.9
2	8 **	0.18	1.74	13.0	37.7	65.6
2	16 **	0.21	1.60	19.6	32.5	54.6
4	18	1.37	2.66	33.4	23.1	
4	47	2.13	1.98	50.4	44.4	
4	48	-	2.42	39.6	-	-
4	72	1.85	2.01	49.7	40.5	-
10	72*	5.15	6.50	36.6	31.0	35.5
4	101	-	1.53	61.8	-	-
4	168	-	0.77	80.7	70.7	96.3

** Water not included in reaction media

* 30-80 mesh - all others through 200 mesh

TABLE 3/6

Glass	Glass Composition %			Polymer	Analysis of products (%)			
Code No.	SiO_2	Al_2O_3	CaO	Yield (%)	I	II	III	IV
191 ALD	36.9	26.8	36.3	89.1	58.8	26.9	13.4	0.9
191 BVJ	6.1	46.2	47.7	10.1	86.6	10.2	3.2	0.0
191 CGS	64.0	9.1	26.0	1.5	92.2	6.5	1.3	0.0
191 CDN	90.0	5.0	5.0	0.9	30.2	43.7	24.4	1.8

[†] internal standardisation.

3.3.5 The trimethylsilylation of mineral silicates using polydimethyl-
siloxanes.

The procedure used was identical to that used in section except
hexamethyldisiloxane was replaced in the trimethylsilylation process by a
series of polydimethylsiloxanes III as shown below in table:

TABLE 3/7

III M.W.	III[+] R_f	Reaction Time (hrs)	Reaction[++] (%)	$\bar{M}_n$	R_f[+++]	C %	H %
236	0.73	37	57.0	536	0.38-0.54	33.4	9.0
680	0.63	39	32.7	848	0.58-0.64	33.8	8.6
1100	0.62	38	5.1	1200	0.55	33.9	8.9
1500	0.57	37	23.9	1768	0.50	32.4	8.2
2500	0.45	36	13.7	2716	0.49	32.0	8.0

The trimethylsilylation of the mineral biotite using polydimethylsiloxanes.

+   major component

++   based on weight of unreacted mineral

+++   highest molecular weight component

3.4   The action of heat on the Polymers

The polymeric material produced by the trimethylsilylation of the mineral
biotite was heated under different conditions.   The polymer was heated
under varied conditions of temperature, pressure, and for different lengths
of time.   In a typical reaction the polymer (2.86g) (Found: C, 30.96%;
H, 8.12%; $\bar{M}_n$ 890), was heated in a drying pistol (200 $^{\circ}$C; 760 mmHg) for
5.0 hours.   The product was a viscous liquid (1.85g) weight loss 35.3%
(Found: C, 27.92%; H, 7.68%; $\bar{M}_n$ 1785).   This residue was analysed by
infrared spectroscopy for hydroxyl groups and the percentage composition
of tetrakistrimethylsiloxysilane and hexakistrimethylsiloxydisiloxane present
in the material was estimated by gas liquid chromatography.   This enabled
the original composition of the original polymer to be established semi-
quantitavely the results of this extensive series of reactions is shown in
Table 3/8.   In further experiments we have investigated the thermal
characteristics by heating in a flow of air and nitrogen gas.   We have
also tried to use a two stage heating process to produce high molecular
weight materials.   These results are shown in tables 3/9 and 3/10.

3.5.   The Reaction of the polymers with low molecular weight species.

3.5.1.   Purification of solvents.

(i)   Hexamethyldisiloxane.

Hexamethyldisiloxane (G.P.R. grade) was distilled prior to use
(b.p.   99.0 - 99.5 $^{\circ}$C; lit. b.p. 100.4 $^{\circ}$C).[15]

(ii)   Carbon tetrachloride

Carbon tetrachloride (G.P.R. grade) was dried for 1 day over
molecular sieve (type 4A).

(iii)   Di-n-butyl ether.

Di-n-butyl ether (G.P.R. grade) was passed down a column of
activated alumina to remove peroxides and then distilled over
a mixture of calcium hydride and sodium (b.p. 138 - 141 $^{\circ}$C; lit.
b.p. 142.2 $^{\circ}$C)[16].

(iv)   Ethanol

Ethanol (G.P.R. grade) was used as supplied.

Table 3/8

Temp (^{o}C)	Press (mmHg)	Wt.loss (%)	Time (hrs)	$\overline{M}_n$	Product C%	H%	Loss I%	II%
45	3	–	5	890	30.96	8.12	0	0
100	3	21.0	5	1342	29.35	7.86	88	30
100	150	28.7	5	1130	29.93	7.82	37	24
100	760	50.0	5	2453*			–	–
200	3	67.5	5	3556	26.00	6.87	100	98
200	3	59.7	10	4128	27.03	7.00	100	100
100	760	2.5	5	901	30.75	8.07	27	59
180	760		2	1302	29.95	8.13	85	36
200	760	35.3	5	1785	27.92	7.67	96	61
235	760	47.0	5	2981	25.85	6.65	100	95
300	760	62.6	5	–†	3.52	1.71	~	–
315	760	32.7	0.5	1029	30.64	7.69	78	73
500	760	68.0	5	–†	0.00	0.00	~	–
700	760	66.0	5	–†	0.00	0.00	~	–
1000	760	57.5	5	–†	0.00	0.00	~	–

*   heating in an air flow

†   insoluble product

I   tetrakistrimethylsiloxysilane

II   hexakistrimethylsiloxydisiloxane

Table 3/9   Heat treatment of biotite polymer

Temp (^{c}C)	Press (mmHg)	Wt.Loss (%)	Time (hrs)	$\overline{M}_n$	Product		Loss	
					C%	H%	I%	II%
100	760	24.8	5					
200	760	44.8	5	1521	28.37	7.51	96	44
300	760	58.6	5	4110	25.99	8.15	100	100
300	760	61.3	30	6924	24.53	6.49	100	100
300	760	65.9	60	− †				
500	760	76.3	5	− †	10.65	3.85	100	100
700	760	85.2	5	− †			100	100

† insoluble product

I   tetrakistrimethylsiloxysilane

II   hexakistrimethylsiloxydisiloxane

Table 3/10

Temp ($^{\circ}$C)	Press (mmHg)	Wt.loss (%)	Time (hrs)	$\overline{M}_n$	Product C%	H%	Loss I%	II%
100	760	2.5	5	1313	29.73	7.89	82	0
200	760	9.1	5	1606	28.76	7.35	96	55
300	760	32.5	5	4401	25.99	7.32	100	100
500	760	77.1	5	— †	11.10	4.42	100	100

†   insoluble product

I   tetrakistrimethylsiloxysilane

II   hexakistrimethylsiloxydisiloxane

The effect of further heat treatment biotite polymer previously heat treated 180 $^{\circ}$C, 760 mmHg for 2 hours ($\overline{M}_n$ 1302)

3.5.2 General method for reacting polymers

Biotite polymer, characterised by elemental analyses for carbon and hydrogen and molecular weight measurement by vapour pressure osmometry, was dissolved in an appropriate solvent. The reagent in solvent was added to the polymer and the mixture stirred under nitrogen at 20 $^{\circ}$C for 4 hours.

The solvent and excess reagent were removed under reduced pressure and the product dried to constant weight in a drying pistol (45 $^{\circ}$C, 3 mmHg). A summary of reaction conditions, elemental analysis for carbon and hydrogen and molecular weight determinations for the products are to be found in tables contained in section 4.

3.6   Redistribution reactions – acid/base catalysis of polyorgano-
       siloxanes.

3.6.1(i) Reaction with base

The polyorganosiloxane derived from the mineral wollastonite was analysed
as follows: (Found: C, 31.5%; H, 8.3%; OH $\approx$ 0.8%; $\overline{M}_n$, 890). The polymer
was heated to temperatures of 140, 180 and 200 $^{\circ}$C in the presence of
potassium hydroxide to give products of molecular weight, $\overline{M}_n$, of 771, 883
and 862 respectively; stirring for ten days at 0 -12 $^{\circ}$C with potassium
hydroxide gave a product of $\overline{M}_n$, 940.

   (ii) Reaction with acid

Similar treatment to the above using sulphuric or hydrochloric acids, in
place of base, gave similar results as summarized below :

Polymer $\overline{M}_n$	Acid	Temp. ($^{\circ}$C)	Time	Polymer Product $\overline{M}_n$
890	H_2SO_4	0 - 12	10 days	958
890	H_2SO_4	200	2.5 hrs.	968

3.6.2   Reaction with hydrochloric acid

Biotite polymer (1.003g, 0.0010 mole) (Found: C, 31.91%; H, 8.15% $\overline{M}_n$, 985)
was refluxed (76 $^{\circ}$C) with concentrated hydrochloric acid (0.526g, 0.014 mole),
(d = 1.18), in dry carbon tetrachloride (20 cm^3) under nitrogen for 24 hours.
The solution of product in carbon tetrachloride was washed with sodium
bicarbonate solution (10%, 5 x 10 cm^3) and dried over molecular sieve (type 4A).
Solvent was removed under reduced pressure and the polymeric material dried
to constant weight (45 $^{\circ}$C, 3 mmHg) to give the product (0.709g), (Found: C,
30.52%; H, 8.22%; $\overline{M}_n$, 814). A blank was performed, (Found: C, 31.08%; H,
8.24%; $\overline{M}_n$, 792).

3.7   Catalytic reaction of polyorganosiloxanes with dimethyldichlorosilane
       in the presence of ferric chloride

(i)   Polyorganosiloxane (10.05g, 0.0113 mole) $\overline{M}_n$, 890) was heated
with dimethyldichlorosilane (10.01g, 0.0776 mole) and ferric chloride (0.1g)
for 22 minutes at a maximum temperature of 70 $^{\circ}$C. The product (19.47g) was
carefully separated into a volatile component (10.41g) and a solid component
(8.77g). The volatile component was characterised by g.l.c. and was shown to
contain trimethylchlorosilane and dimethyldichlorosilane in the ratio 9:1.

The solid component was insoluble in organic solvents (Found: C, 10.76%;
H, 4.96%; Cl, 13.9%). Further reactions gave soluble products, see Table 2.4/1.

3.8   The reactions of the trimethylsilyl groups.

3.8.1 Chlorination of wollastonite polymer.

Wollastonite polymer (15.01 g, 0.0169 mole), (Found: C, 31.5%; H, 8.3%;
OH, $\approx$ 0.8%; $\overline{M}n$, 890) was dissolved in dry carbon tetrachloride (50 cm^3)
and placed in the reaction vessel. The apparatus was flushed with
nitrogen for 10 minutes. A tungsten lamp (250 W) was positioned at
a distance of 3" from the reaction vessel; chlorine gas was passed
through the polymer solution ($\approx$ 15 cm^{3}min^{-1}) which was stirred for
4 h. After the reaction the lamp was switched off and as the product
solution cooled the product was transferred to a round bottomed flask
and dissolved chlorine removed at the pump (20 $^{\circ}$C, 17 mmHg).
Solvent was removed (60 $^{\circ}$C, 17 mmHg) and the product dried (45 $^{\circ}$C, 3 mmHg)
to constant weight (14.33 g), (Found: C, 22.02%; H, 4.70%;Cl, 32.26%;
$\overline{M}_n$, 1166).The product, chloro-wollastonite polymer, was a yellowish
heavy viscous liquid.

3.8.2   Conversion of chloro-wollastonite polymer to the acetoxy derivative.

Chloro-wollastonite polymer was converted to its acetoxy derivative using the method of Speier et al (17).   Polymer (5.00g, 0.0043 mole), $\overline{M}_n$, 1166) was weighed into the reaction vessel and glaciel acetic acid added (25 cm^3). Anhydrous potassium acetate (1.98 g, 0.0203 mole) was then added and the mixture was refluxed for 24 h. After reaction the mixture was allowed to cool and dissolved in ether (75 cm^3). The product solution contained a white solid which was filtered, washed with ether and air dried, (1.11 g). The solid was analysed for chlorine using the Volhard method (Found: Cl, 49.02%; KCl requires Cl, 47.65%). The filtrate was extracted with water (10 x 20 cm^3) until neutral. The aqueous extracts were combined, diluted to 500 cm^3 in a graduated flask and estimated for chlorine (Found: Cl, 0.1 g). The ether layer was dried using a molecular sieve (type 4A). Solvent was removed (20 ^{o}C, 17 mmHg) and the product was dried to constant weight. (Found: C, 28.59%; H, 6.89%; $\overline{M}n$, 953). The product, acetoxy-wollastonite polymer, was a greyish mobile liquid considerably less viscous than chloro-wollastonite polymer.

3.8.3   Conversion of acetoxy-wollastonite polymer to the hydroxy derivative
Acetoxy-wollastonite polymer was converted to its hydroxy analogue using the method of Speier et al (17). Methanol (150 cm^3, G.P.R. grade) was dried over a molecular sieve (type 4A). Hydrogen chloride gas (prepared by the slow addition of concentrated sulphuric acid to sodium chloride) was passed through the methanol for 2h. The acidity of the methanol (2.1 M) was estimated using standardised sodium hydroxide solution.

Acetoxy-wollastonite polymer (1.7907 g, 0.0019 mole) was added to the reaction vessel and acidified methanol solution (25 cm^3) added. The mixture was stirred at ambient temperature (20 ^{o}C) for 96 h with a calcium chloride guard tube attached to the apparatus. Solvent, which contained methyl acetate formed from the acetoxy groups which had been replaced on the polymer, was removed by evaporation (65 ^{o}C, 760 mmHg) and retained for further examination.

The solvent was diluted to 25 cm^3 in a graduated flask with dry
methanol and the methyl acetate concentration (320 mg) was estimated
by ultraviolet spectroscopy (λ_{max}, 229 nm). The polymeric product
was dissolved in ether (50 cm^3) and extracted with water (20 cm^3).
Further extractions were made until the washings were neutral
(3 x 10 cm^3). The ether layer was dried over a molecular sieve
(type 4A). The ether was removed at the pump (20 ^{o}C; 17 mmHg) and
the product was dried (45 ^{o}C, 3 mmHg) to constant weight (0.6900 g),
(Found: C, 20.38% ; H, 4.05% ; $\bar{M}_n$, 1211). The product, as
hydroxy-wollastonite polymer, was greyish viscous liquid considerably
more viscous than acetoxy-wollastonite polymer.

3.8.4. Reaction of hydroxy-wollastonite polymer with trichlorovinylsilane.

Hydroxy-wollastonite polymer (0.2791 g, 0.0002 mole), (Found: C, 20.38% ;
H, 4.05 % ; $\bar{M}_n$, 1211) was dissolved in dry carbon tetrachloride (5 cm^3)
and placed in the reaction vessel. Trichlorovinylsilane (3.2008 g,
0.0198 mole) in dry carbon tetrachloride (10 cm^3) was added to the
polymer and the mixture was stirred under nitrogen at ambient
temperature (20 ^{o}C) for 4 h. The solvent and unreacted silane were
removed (60 ^{o}C, 17 mmHg) and the product was dried to constant weight
(0.2882 g), (Found: C, 13.33% ; H, 5.40% ; $\bar{M}_n$ 1405). The polymer was
found to contain chlorine by qualitative analysis. The product was
a reddish elastomer material which became brittle on ageing.

4.   TABLES OF DATA

Table 4/1 : <u>The reaction of polyorganosiloxanes with organic molecules.</u>

Reactants	Major Peak (S)	Solvent
Thuringite resin, PhNCO	1119	ODCB
Thuringite resin SOCl$_2$	669	ODCB
Phlogopite resin PhNCO	1019	ODCB
Biotite resin, Ph$_2$PCl	1646	ODCB
Thuringite resin, Ph$_2$PCl	196, 925, 2650	THF
Thuringite resin, MeCOCl	700, 2150	THF
Biotite resin, PhNCO	700, 925, 3449	THF
Biotite resin, MeCOCl	700, 3449	THF
Biotite polymer, SOCl$_2$	700, 2650	THF

Table 4/2 : Reactions of the polymers derived from the mineral biotite

Wt. of Polymer (g)	Wt. of reactant (g)	Wt. of product (g)	M.W. Polymer	M.W. Product
10.00	Me_3SiCl (1.5)	10.62	1161[1] 760	-
2.6	Me_3SiCl (1.0)	1.74	1161 760	-
2.0	$SOCl_2$ (1.27)	1.50	760	700[*] 2650[*]
2.0	MeCOCl (0.21)	1.60	760	700[*] 3449[*]
1.0	PhNCO (0.21)	0.72	760	700[*] 925[*] 3449[*]
1.0	Ph_2PCl (0.39)	1.16	760	1646

Reactions of the polymers derived from the mineral phlogopite

| 1.60 | Me_3SiCl (1.0) | 1.50 | 684 | |
| 1.42 | PhNCO (0.49) | 1.15 | 684 | 1019 |

Reactions of the polymers derived from the mineral thuringite

2.9	Me_3SiCl (1.5)	3.11	906	
1.0	$SOCl_2$ (0.39)	0.82	906	669
1.0	PhNCO (0.26)	0.90	906	1119
1.0	MeCOCl (5.0)	-	906	700[*] 2150[*]
1.0	Ph_2PCl (0.5)	-	906	196[*] 925[*] 2650[*]

1 - by vapour pressure osmometry.

[*] All other molecular weights were determined by gel permeation chromatography in o-dichlorobenzene except for those asterisked which were carried out in tetrahydrofuran.

Table 4/3   Elemental analyses of starting materials and products

	Polymer			Reactant	Product		
	C%	H%	Si%		C%	H%	Si%
Biotite	31.9	7.2	36.3	Me_3SiCl	33.9	8.2	40.6
Biotite	26.1	6.3	33.6	Me_3SiCl	21.7	4 2	
Thuringite	31.5	7.7	38.8	Me_3SiCl	28.7	7.1	
Phlogopite	30.9	7.3	36.2	Me_3SiCl	33.3	10.3	
Biotite	31.9	7.2	36.3	$SOCl_2$	30.9	7.7*	
Biotite	31.9	7.2	36.3	CH_3COCl	32.0	8.0*	
Thuringite	31.5	7.7	38.8	CH_3CCl	31.4	7.9*	
Thuringite	31.5	7.7	38.8	Ph_2PCl	44.8	6.8	

* The presence of sulphur, chlorine was not detected.

Table 4/4   Reaction of hydroxyl groups bound to a polyorganosiloxane

Wt. of biotite polymer	C%	H%	$\overline{Mn}$	Reactant (g)	Wt.(g)	Product			
						C%	H%	$\overline{Mn}$	Cl
1.0	29.36	7.57	1406	Me_3SiCl (10.0)	0.883	29.38	7.59	1622	
0.51	28.71	7.33	1981	Cl_3ViSi (10.4)	0.672				
1.01	31.91	8.15	985	Cl_2Me_2Si (9.86)	0.922	28.71	7.82	1418	- ve
0.98	31.91	8.15	985	$Cl_2MeViSi$	0.931	30.82	7.19	1364	+ ve
0.93	31.91	8.15	985	Cl_3ViSi (10.70)	0.836	20.82	7.54	1148	- ve

Table 4/5

Reaction conditions for the polymers derived

from the mineral biotite

Wt of polymer (g)	Molarity Polymer	Reactant (g)	Molarity reactant	Solvent (cm^3)	Temp (^{o}C)	Time (HR)	Drying Conditions (^{o}C, mmHg)
0.728	0.00052	BzCl (7.300)	0.058	*HMD (20)	20	24	65, 1.5
0.973	0.00049	Cl$_2$Me$_2$Si (10.877)	0.084	CCl$_4$ (50)	20	4	45, 3
0.981	0.00050	Cl$_2$MeViSi (9.947)	0.071	CCl$_4$ (50)	20	4	45, 3
1.014	0.00051	Cl$_3$ViSI (10.431)	0.065	CCl$_4$ (50)	20	4	45, 3
† 0.532	0.00027	PhPOCl$_2$ (0.549)	0.0028	CCl$_4$ (30)	20	4	-

* Hexamethyldisiloxane

† Sample not dried injected in solution into hplc.

Table 4/6

Elemental analysis and molecular weights of
starting materials and products

Polymer				Reactant	Product			
Wt taken (g)	C %	H %	$\overline{Mn}$		Wt(g)	C %	H %	$\overline{Mn}$
Biotite 0.728	29.36	7.57	1406	BzCl	0.332	27.84	7.49	2396
Blank –	29.36	7.57	1406	–	–	28.28	7.58	1623
Biotite 0.973	28.71	7.33	1981	Cl_2Me_2Si	0.973	28.64	7.22	1941
Biotite 0.981	28.71	7.33	1981	$Cl_2MeViSi$	0.920	28.32	7.22	1659
Biotite 1.014	28.71	7.33	1981	Cl_3ViSi	0.873	28.64	7.06	2059
Blank –	28.71	7.33	1981	–	–	–	–	1711

REFERENCES

1. C.W. Lentz, Inorganic Chemistry, 1964, 3, 574.

2. B.R. Currell, H.G. Midgley, M.A. Seaborne and C.P. Thakur,
    British Polymer Journal, 1974, 6, 229.

3. R. Atwal, C.B. Cook, B.R. Currell, H.G. Midgley and J.R. Parsonage.
    Coatings and Plastics Preprints 1977, 37(1), 67.

4. J.P. Birchall, J.G. Carey and H.J. Howard, Nature, 1977, 266, 154.

5. K.A. Andrianov and V.M. Mantrova, Zhur. Obschchei. Khim., 1957, 27,
    1234. C.A. 1958, 52, 3668.

6. R.H. Krieble and J.R. Elliot, J.A.C.S., 1946, 68, 2291.

7. R.H. Krieble and J.R. Elliot, J.A.C.S., 1945, 67, 1810.

8. J.M. Sosa, Thermochimica Acta., 1975, 13, (1), 100.

9. S.Siggia, Quantitative Organic Analysis via functional groups, Wiley,
    New York, 1943.

10. D. Von Hoebbel and W. Wieker, Z. Anorg. allg. Chem., 1974, 405, 163.

11. F.F.H. Wu, J. Gotz, W.D. Jamieson and C.R. Masson,
    J. Chromatography 1970, 48, 515.

12. I.Y. Borg and D.K. Smith, Calculated X-ray Powder Patterns for Silicate
    Minerals, Geological Soc. of America, Boulder Colorado, USA 1969.

13. B.D. Saksena, Trans. Faraday Soc., 1961, 57, 242.

14. V.P. Ivanora, Zapisk. Vses. Min. Obsh., 1961, 90, 50.

15. C. Eaborn, Organosilicon compounds, Butterworths, London 1960.

16. J.A. Riddick and W.B. Bunger, Organic solvents, physical properties
    and methods of purification, Wiley, New York, 1970.

17. J.L. Speier, B.F. Daubert and R.R. McGregor, J.A.C.S., 1949, 71, 1474